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Technical Note N-1353

THE FATE OF SPILLED NAVY DISTILLATE FUEL

By

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Laboratory weathering studies of four Navy distillate fuels on salt water showed that in thick films (5 mm) the major portions of the oils (75 to 90%) did not evaporate in one week. These fuels are thus relatively persistent oils. The physical properties did not change markedly and the thick emulsion, or mousse, obtained with Navy special fuel oil was not obtained with the distillate fuels. Very thin films (0.1 mm) evaporated

continued

20. Continued

much more rapidly, leaving residues of about 5%, whereas Navy special fuel oil left residues of 65%. The weathering characteristics are related to the distillation range as shown by gas chromatographic comparisons.

CONTENTS

INTRODUCTION

        As the Navy is changing from the use of Navy special fuel oil
(NSFO) to the use of Navy distillate fuel it becomes more important
to know the fate of distillate fuel when it is spilled at sea. Of
particular interest are the persistence of the oils at sea and the
properties and changes in properties that are related to the removal
of the oil by man or by natural means.
        The general changes that take place in crude oils on the open
sea are known [1]. Evaporation and dissolution studies of several
fuel oils have been reported recently [2]. Comparatively little specific
information is available about the weathering of Navy distillate
fuel. The distillate fuel is expected to evaporate faster than the
NSFO and is expected not to become as viscous as spilled NSFO, but
how great these differences are is not known. The lack of color will
make recovery operations more difficult. An investigation at the Civil
Engineering Laboratory[a] (CEL), Naval Construction Battalion Center,
Port Hueneme, CA, was, therefore, sponsored by the Navy Supervisor
of Salvage.
        Samples of various Navy distillate fuels and of NSFO were subjected
to simulated ocean weathering in the laboratory. The results of this
investigation are presented in this report.

EXPERIMENTAL WORK

Properties of the Fuel Oils

        Five fuel oils were obtained for the experiments. Four of these
were Navy distillate fuels, which were designated Fuel Oils A, B,
C, and D; the fifth was a Navy special fuel oil, designated Fuel
Oil E. Some of the properties of the distillate fuels and the corresponding
specification values [3], with degrees Fahrenheit converted to degrees
Centigrade, and with API gravities also listed as specific gravities,
are shown in Table 1.
        The colors of the fuels ranged from a light brownish amber (1.0)
to a dark reddish brown (3.5). The reported crude sources were: Oil
A - 100% Arabian Crude; Oil B - 30% Southern California Regular, 14%
Torrance and Wilmington, 20% Inglewood, and 36% Segregated; Oil C - 79%

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[a] Formerly Naval Civil Engineering Laboratory.

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Table 1. Selected Properties of Distillate Fuels

Properties	Fuel Oil				Specifications
	A	B	C	D	
Viscosity, Kinematic, at 38°C (100°F), centistokes	2.83	3.10	4.4	3.81	10.0 maximum
Density, at 16°C (60°F):					
Specified Gravity	0.832	0.857	0.874	0.865	0.893 maximum
API Gravity	38.5	33.6	30.4	32.1	27 minimum
Color, ASTM	1.0	3.5	2.5	1.5	-
Distillation, $^\circ$C					
10%	238	237	257	224	260 maximum
50%	274	281	289	281	341 maximum
90%	334	317	318	337	393 maximum
95%	349	327	325	349	407 maximum

Cal-Mix, 21% Murban; Oil D - 35% Los Angeles Basin, 23% Light Mix
(Northern California), and 42% Iranian.

The NSFO had a much higher viscosity of 48 cs (at 122°F or 50°C);
its specific gravity was 0.984 and its API gravity 12.3; it was black;
and it was of unknown prior history.

The distillate fuels were subjected to gas chromatography to
determine the approximate boiling point distribution of the fuel
components. The gas chromatographic analyses were made according
to ASTM D 2887-70, using conditions similar to those proposed by
R. E. Kreider [4]. Dual 10-ft, 1/8 in., stainless steel columns with
10% OV-101 on 80/100 mesh Chromosorb W (AW-DMCS) were used. The tempera-
ture was programmed from 75°C to 325°C at a rate of 8° per minute
with a 3-minute post-injection delay and a 12-minute upscale delay.
The injector temperature was 300°C, and the hydrogen flame detector
temperature was 350°C. Samples of about 3 microliters were used with
helium flow at 40 ml per minute and an attenuation of 10^3 x 16. The
positions of the normal alkanes were identified by comparison with
a chromatogram of a distillation calibration sample.

As is evident from the gas chromatograms shown in Figures 1a, 2a, 3a and 4a, Fuel Oil D had the highest proportion of low boiling components, whereas Fuel Oil C had the lowest proportion of low boiling components. All of the distillate fuels had negligible components with more than about 22 carbon atoms. Fuel Oil C had a very narrow boiling range; it not only had the lowest proportion of low boiling components, but it also had the lowest proportion of high boiling components, which included very little material with over 20 carbon atoms.

Evaporation of Thin Oil Films

Samples of the fuel oils were put into flat weighing dishes and these were placed in a current of air and were weighed periodically. The fifty-milligram samples of the oils, with specific gravities of about 0.85, have volumes of about 59 microliters; and in dishes 25 mm square, these should form films slightly under 0.1 mm thick. The dishes were placed at the opening of a partly closed fume hood and they were rotated after each weighing to provide nearly equal exposure for each oil. The temperature of the room was approximately 25°C. The percentages of the oils remaining are shown in Table 2, and are plotted in Figure 5.

Table 2.   Evaporation of Thin Films

Fuel Oil	Percentage of Oil Remaining After					
	1/4 day	1 day	2 days	3 days	6 days	8 days
A	70	40	23	15	4.3	3.9
B	63	43	26	16	3.0	2.4
C	82	58	42	33	5.0	1.9
D	64	44	29	17	5.5	5.4
E	83	73	69	68	64	64

Simulated Weathering of Oils on Seawater

The simulated weathering was performed in a 12-liter three-necked flask filled to the halfway mark with 6 liters of 3% aqueous sodium chloride. The apparatus is shown in Figure 6. The diameter of the flask was 29 cm, and therefore the surface area of the salt water was 660 sq cm. A weighed 330-ml portion of the fuel oil was added to provide a 5-mm layer of oil.

Air was supplied, at a flow of 6 liters per minute, through an inlet tube reaching near the bottom of the flask. This air was first freed of oil by filters and was saturated with water by a fritted glass bubbler. Wind was provided by a paddle 15 cm wide and 4.5 cm high, suspended above the oil layer and rotated at 600 rpm. The circumference of the paddle was 47 cm. Since one mile per hour is 44.7 cm per second, one revolution per second provides a speed of about 1 mile per hour at the paddle tip. At 600 rpm, the wind speed at the paddle tip was thus about 10 miles per hour.

A preliminary run was made with Fuel Oil C. This run was allowed to progress for 44 days, during about 15 of which the stirring motor was inoperative, and no wind was produced. All the other weathering experiments were run for 7 days, with wind. One exception was a second weathering of Oil D which was performed without wind.

At the completion of each run, the distillate fuel oil and the water were allowed to separate for several hours. The bulk of the weathered oil was then syphoned off through a glass tube, which was inserted in one of the necks of the flask. This tube was flared at the bottom and barely touched the surface of the oil. A slight vacuum was used to lift the oil out of the flask and transfer it into a weighed bottle. The bulk of the salt water was then removed from the flask through the air inlet tube. A vacuum was applied, and the salt water was collected in a filter flask. The remainder of the oil and water was mixed with hexane, and the resulting hexane solution was washed with water and evaporated. The evaporation of the hexane was completed by placing the flask containing the oil into a water bath at 80°C and passing 400 ml per minute of dry nitrogen through the oil for 1 hour after escaping vapors of hexane were no longer visible.

The weathered NSFO did not coalesce well and could not be syphoned off. It was recovered by decanting repeatedly over a period of several days until no more salt water separated. The residual oil and water mixtures were extracted with dichloromethane, and the dichloromethane solution was washed and evaporated in the water bath under nitrogen flow.

The amounts of original and recovered oil are shown in Table 3.

The weathered distillate fuels were subjected to gas chromatography under the same conditions described above (under Properties of Fuel Oils). The chromatograms obtained for the four fuel oils after 1 week of weathering with wind are shown in Figures 1b, 2b, 3b and 4b.

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Table 3. Weight Changes During Weathering

Fuel Oil[a]	Original Oil (gm)	Weathered Oil (gm)			Percentage Recovered
		Syphoned	Extracted	Total	
A	268.8	175.8	41.3	217.1	80.0
B	277.7	142.1	68.2	210.3	75.7
C	280.8	183.9	69.2	253.1	90.1
D	278.4	115.9	99.7	215.6	77.4
D[x]	281.7	198.6	47.2	245.8	87.2
C[y]	285.9	158.0	55.4	213.4	74.7
E	317.4	159.6[b]	132.3	291.9	92.0

[a] x = Weathering without wind.
 y = Preliminary 6-week experiment.

[b] Separated by decanting.

The areas of the curves were measured with a disc integrator. The total areas and the areas above a boiling point of 298°C are shown in Table 4; also shown are the calculated portions remaining after weathering and the percentages of oils recovered as given in Table 3.

The viscosities of the oils were determined with a Zeitfuchs Cross-Arm viscometer held in a bath at 22.2°C (72°F). For the distillate fuels a Number 2 viscometer was used. For the NSFO a Number 4 viscometer was used. The viscosity changes are shown in Table 5.

Total organic carbon analyses of the salt water extracts were made. The values obtained for the aqueous layers from the weathering of the oils are shown in Table 6.

DISCUSSION

General Considerations

Many factors will affect the fate of fuel oil spilled on the open sea: wind; agitation; temperature; sunlight; micro-organisms; presence of foreign matter; and, of course, the composition of the

Table 4. Oil Remaining After Weathering

(Calculated from gas chromatographic data and
compared with the weight percentages recovered)

Oil[a]	Integrated Area[b]		Portion Remaining (P)[c]	Recovered Oil (%)
	Total (A)	Above 298°C (A_n)		
A^o	23,620	6,660	–	–
A^w	21,270	7,480	0.802	80.0
B^o	36,090	12,190	–	–
B^w	27,740	12,040	0.778	75.7
C^o	34,220	15,620	–	–
C^w	33,410	16,710	0.913	90.1
C^y	19,000	11,100	0.781	74.7
D^o	36,640	14,870	–	–
D^w	29,610	15,660	0.767	77.4
D^x	31,010	14,130	0.891	87.2

[a] o = original.
w = weathered.
x = weathering without wind.
y = preliminary 6-week experiment.

[b] Disintegrator count.
[c] Calculated from $P = (A^w/A^o)(A_n^o/A_n^w)$.

Table 5. Viscosity Changes During Weathering

Fuel Oil[a]	Viscosity at 22.2°C (cs)		Viscosity Ratio	Recovered Oil (%)
	Original Oil	Weathered Oil		
A	4.03	4.85	1.20	80.0
B	4.56	6.15	1.33	75.7
C	7.22	8.12	1.12	90.1
D	5.46	7.94	1.45	77.4
D^x	5.46	6.65	1.22	87.2
E	271	882	3.25	92.0

[a] x = Weathering without wind.

Table 6. Carbon Content of Aqueous Extracts

Fuel Oil[a]	Total Carbon (ppm)	Inorganic Carbon (ppm)	Organic Carbon (ppm)
A	16.0	1.1	14.9
B	38	1.1	37
C	22.5	1.5	21.0
D	23.0	0.7	22.3
C^y	54-1/2	2.6	52
E	15.8	1.3	14.5

[a] y = Preliminary 6-week experiment.

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fuel oil. The changes that will take place in the oil include the loss of light components by evaporation and the loss of constituents by dissolution or dispersion. Chemical changes caused by oxidation or photodegradation can produce oxygenated compounds, volatile products, and condensation products; and additional chemical changes can result from biodegradation. The presence of polar products and heavier components may produce emulsification, and heavier components combined with foreign matter may produce settling. Spreading will produce thinner films in which all the above processes may be speeded up.

Chemical decomposition of distillate fuels, including decomposition by microorganisms, is a comparatively slow process. Although chemical or biological processes may be effective in removing final traces of dispersed fuels, they are not expected to contribute materially to the removal of the bulk of the oils. Dissolution is also expected to be a minor factor in oil removal because of the very low solubilities of hydrocarbons in water.

The chief method of loss of oil over a relatively short time span, of perhaps a week or less, is expected to be by evaporation. The rate of evaporation will depend on the vapor pressure of the oil, on the thickness of the oil, on the temperature, and on the wind speed.

Vapor Pressure. The vapor pressure of fuel oil depends on the components that are present. The hydrocarbons with the lowest number of carbon atoms have the lowest boiling points and the highest vapor pressures. As the numbers of carbon atoms of the hydrocarbons increase, the boiling points increase and the vapor pressures decrease. A fuel with larger amounts of lower hydrocarbons will have a higher vapor pressure and will evaporate faster. The lower boiling hydrocarbons will tend to evaporate first, and the vapor pressure and the rate of evaporation will then decrease.

All distillate fuels have at one time been evaporated during the distillation process. The vapor pressures of all the components are thus sufficiently high that essentially all spilled distillate fuel that is not otherwise removed would eventually be lost by evaporation. Residual fuels, such as NSFO, consist primarily of components having negligible evaporation rates. Therefore, a comparatively small amount of the NSFO would be lost by evaporation.

Thickness. The thickness of an oil slick is an important factor in its evaporation rate because the evaporation takes place at the surface of the film. At a given moment, the amount of oil evaporated is not affected by the depth of the oil, and the percentage loss is therefore much greater for a thin film with a high surface-to-volume ratio. Over a period of time, the composition at the surface will change to less volatile components and the more volatile components will migrate to the surface from the interior of the oil layer. This process is more rapid in a thinner layer or in agitated oil.

Temperature. The temperature will affect the evaporation rates because it affects the vapor pressures of the components. The temperature also affects the viscosity of the oil and the rate of migration of the components. However, the range of ocean temperatures is limited, and the effect of temperature is expected to be small compared to the effect of differences in composition.

Wind. Wind will affect the evaporation rate because it provides fresh air that is not already partly saturated by the components of the oil. In a completely stagnant situation an equilibrium would be created in which all components would be present in the air in direct proportion to their vapor pressures, and any net additional evaporation would cease. Rapidly moving fresh air will prevent any approach to saturation and will have the same net effect as an increase in vapor pressure.

Evaporative Losses

The experimental results were in agreement with the above considerations. The evaporation experiments with thin films of fuel oils show that under rapidly moving fresh air the major portions of the distillate fuels will evaporate. About 95% or more of the distillate fuels were lost in a week under these conditions, whereas only 33% of the NSFO was lost, as shown in Figure 5. However, the thickness of these fuel oil films was only 0.1 mm, and much lower evaporation rates would be expected for thicker films.

In the simulated weathering of Navy distillate fuels spilled on seawater, the fuel losses in one week were from about 10% to about 25%. The oil thickness in these experiments was 5 mm. The thickness of a typical oil spill might be about half this thickness.

The thickness of an oil spill will vary, of course. In a controlled spill of No. 2 fuel oil there was reported to be a compact region of oil 2.4 ± 0.3 mm thick, surrounded by a thin region only 0.002 to 0.004 mm thick [5]. The thick region contained more than 90% of the oil in less than 10% of the area of the visible slick. According to the specifications, No. 2 fuel oil [6] is a slightly lighter oil than Navy distillate fuel [3], but fuel oils A to D exhibited properties very close to, or within the range, specified for No. 2 fuel oil. Thus, the evaporation characteristics of a typical spill of Navy distillate fuel are likely to be closer to those of a 5-mm layer, which is about twice as thick, than to a 0.1-mm layer, which is about one twentyfifth the thickness of the bulk of the reported spill.

One reason for using an oil thickness of 5 mm in the simulated weathering was to have sufficient oil residues to study their properties. A second reason for using a relatively thick layer of oil was to have enough material to collect the bulk of the weathered oil directly without a complicated recovery system.

In the weathering experiments with the distillate fuels it was fortunately possible to recover most of the evaporated oil by simply syphoning it off the top of the salt water. In the collection of the remainder of the oils by extraction with hexane and subsequent removal of the hexane (to determine the total recovered oil) there were slight additional losses, but experiments indicated that these losses were less than 1% of the extracted portion of the weathered oils.

A method similar to that used in the present experiments had been used by Smith and MacIntyre [2]. These authors had used one tenth as much oil, twice as much salt water, and one third of the airflow. They collected the volatile constituents that were carried off in the airstream by condensing them in a cooled trap. The collected volatile material was dissolved in pentane and subjected to gas chromatography; and, from the area of the oil peaks of the gas chromatogram, the weight of volatile material was calculated. Smith and MacIntyre considered the volatiles to be those components boiling at temperatures not higher than $271^{\circ}C$, the boiling point of pentadecane (C_{15}). They also sampled oils from controlled spills and from the peak heights determined the losses of individual hydrocarbons. They found that the losses in volatiles were much more rapid in oils spilled at sea, especially when there was wind, and that the volatiles lost at sea included much higher proportions of C_{14} and C_{15} hydrocarbons.

In the present investigation, the weathering was increased by adding the effect of wind produced with a paddle. The airflow was increased also, but increased airflow alone would have much less effect than the use of the paddle. Airflow introduced at the bottom of the flask pushes aside the oil, and increased airflow produces relatively little increased contact.

Gas chromatography is a commonly used technique in the study of petroleum products, because it gives considerable information about the composition of the relatively volatile components. The components come off the column in order of volatility or boiling points (as shown in Figures 1 to 4), and the areas under the peaks are proportional to the amounts of the various components. To a lesser degree, the peak heights are also proportional to the amounts present. Both of these relationships have been used for quantitative calculations. Thus, Smith and MacIntyre have calculated the losses of specific hydrocarbons from fuel oils [2], and Sivadier and Mikolaj have calculated the loss of volatiles from crude oil slicks [7].

The data from the gas chromatography of the original and weathered Navy distillate fuels was used to calculate the portion of oil remaining after weathering. For these calculations, the components boiling below $298^{\circ}C$ were considered to be volatile, and the components boiling above $298^{\circ}C$ were considered to be nonvolatile. The calculated results for 1-week simulated weathering agree within 2% with the amounts of oil that were recovered, as shown in Table 4. For the longer weathering of Oil C, the deviation was greater.

The initial evaporative losses of spilled Navy distillate fuels can thus be determined rather closely by a comparison of the gas chromatograms of the original and weathered oils. The losses on more extended weathering cannot be determined as accurately. Partly this is due to the fact that there is no discrete demarcation between the ''volatile'' and ''nonvolatile'' portions of the oils. Instead, there is a wide range of volatility of the many components.

The significance of the gas chromatographic results and the calculations that were made are further discussed in the Appendix.

A comparison of the gas chromatograms with the thin film evaporation experiments indicates that the weight loss in short term weathering is greater for oils with a greater portion of low boiling components. On the other hand the persistence of thin films is greater for oils with a greater portion of high boiling components. Thus, Oil C evaporated least rapidly in the simulated weathering experiments and in the beginning of the thin film evaporations. However, the same oil evaporated most rapidly at the end of the thin film evaporations; and, in that sense, it was the least persistent of the oils.

All of the four Navy distillate fuels had distillation temperatures considerably below the specification requirements. Thus, other Navy distillate fuels could be within the specification but because of higher distillation temperatures, they could be appreciably less volatile and more persistent.

Dissolution and Dispersion

Fuel oils spilled at sea will also sustain losses due to dissolution and dispersion; but, based on investigations reported in the literature, it is expected that these losses ordinarily would be small and would not appreciably reduce the bulk of the oil. There is a concern, however, that significant amounts of toxic components might be disseminated in the aquatic environment [8].

The solubility of hydrocarbons decreases with increasing molecular weight [9]. It is comparatively low for aliphatic hydrocarbons, being less than 1 ppm for normal octane. The solubility increases with increased unsaturation and is considerably higher for aromatic compounds. The solubility is about 50 ppm for isopropylbenzene, but it is lower for the higher molecular weight aromatics present in fuel oils. The aromatic components are not only more soluble than the aliphatic components, but are also more toxic [8]. In one investigation, the seawater extracts of kerosene and of a crude oil contained about 1 ppm aromatics [8]. In another investigation, a maximum of 13 ppm of organic material was extracted from No. 2 fuel oil in a closed static system [10].

The dissolution of fuel oil at sea, in a dynamic system, is a complicated problem beyond the scope of the present investigation. A higher organic content of the seawater might be produced by the presence of dispersed material, rather than dissolved material, which may be difficult to distinguish. The small amounts of volatile compounds originally dissolved might be removed comparatively rapidly by aeration.

Components of the oil that are dispersed into water will become more volatile because their vapor pressure is effectively augmented by that of the water, and a ''steam distillation'' will occur. Similarly, the presence of water should effectively augment the vapor pressure of the bulk oil and speed its evaporation, especially where there is a turbulent interface.

The salt water extracts from the simulated weathering experiments contained 14.5 to 37 ppm of organic carbon, as shown in Table 6, and thus about 17 to 44 ppm of organic compounds. These are higher concentrations than expected on the basis of the literature quoted above, but lower concentrations than obtained in two unpublished investigations. Because the salt water extracts were very clear, it is doubtful that the increased organic content was due to dispersed material. It is more likely that the increased organic content was due to the presence of oxygenated organic compounds that might have been formed by the aeration of the fuel oils. The total dissolved organic compounds, extracted from the 330-ml portions of the oils by the 6-liter portions of salt water (a ratio of 1:18), constituted 0.037% to 0.093% of the original oils. These figures are very close to the 0.053% of dissolved oil that Smith and MacIntyre found in their weathering of 30 ml of No. 2 fuel oil in contact with 10 liters of salt water (a ratio of 1:333) [2].

Changes in Viscosity

The viscosity changes of the Navy distillate fuels in the simulated weathering were not very great. The values in centistokes increased by a maximum of 45%, as shown in Table 5. This change is equivalent to the change obtained when the temperature of the oils is lowered from about 22°C to 10°C (or from about 70°F to 50°F). This is the temperature change that would give the same increases in viscosity according to graphs on standard viscosity-temperature charts [11]. An oil evaporated to the same extent at sea might pick up foreign matter, and the viscosity might thus increase somewhat further.

Navy special fuel oil exposed to the same simulated weathering gave very different results. These differences apparently were caused by the greater viscosity of the NSFO, by its greater density, and probably by the presence of more polar constituents. The agitation of the NSFO was not as effective. A thick emulsion of NSFO and salt water was formed which broke into clumps but did not form very small particles in the salt water. When the aeration was stopped, this ''mousse'' formed a layer about 30 mm thick and did not change in thickness for four days. The distillate fuels, on the other hand, had separated and coalesced rapidly.

The results with the NSFO are not as reliable as those with the distillate fuels because of experimental difficulties. About half of the evaporated NSFO was recovered by decanting and the remainder by extraction with dichloromethane and subsequent evaporation. However, there were unavoidable losses and the residue was probably greater than the indicated 92%. The viscosities of the NSFO could be measured only

approximately with the available apparatus. Although the viscosity change of about three-fold was larger than that of the distillate fuels, this change again was equivalent to only a 12°C (or 20°F) temperature change when plotted on a viscosity-temperature chart. However, this change occurred with a smaller evaporation loss. Also, this was the viscosity of the recovered NSFO, and the viscosity of the ''mousse'' might have been higher.

CONCLUSIONS

1. Navy distillate fuels are relatively persistent oils and do not evaporate rapidly in thick films.

2. Initial weathering of thick films of spilled Navy distillate fuel should not materially change the amount of oil that must be salvaged. In simulated weathering of 5-mm fuel oil films on salt water for one week, the Navy distillate fuels left residues of 75% to 90% of the original oils.

3. Initial weathering of thick films of spilled Navy distillate fuel should not materially change the handling characteristics of the oils. Simulated weathering of 5-mm fuel oil films on salt water produced small increases in viscosity and small changes in boiling range.

4. Very thin films of Navy distillate fuel will evaporate much more rapidly than Navy special fuel oil. Navy distillate fuels exposed in 0.1-mm films under a current of air for one week, left residues of about 5%, whereas the Navy special fuel oil left a 65% residue.

5. The weathering characteristics of distillate fuels can be correlated with their gas chromatographic behavior. Oils with greater portions of low boiling components (below about C_{15}) will have higher initial losses, and oils with greater portions of high boiling components (above about C_{20}) will leave greater residues.

6. In simulated laboratory weathering, the persistent emulsion formed with Navy special fuel oil is not formed with Navy distillate fuel.

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APPENDIX

DETERMINATION OF OIL EVAPORATION BY
GAS CHROMATOGRAPHY

Gas chromatography can be used to estimate the losses of volatile components from fuel oils or crude oils. The following calculations form the basis for the brief discussions in the body of the report.

If it is assumed, as a simplification, that a mass of oil, M, is composed of a volatile portion, M_v, and a ''nonvolatile'' portion, M_n, then

$$M = M_v + M_n \tag{1}$$

If the nonvolatile portion is sufficiently volatile to be gas-chromatographed readily, and if the above masses are proportional by a factor, a, to the respective areas, A, in the gas chromatogram of the original oil, ^{O}, then

$$M^O = M_v^O + M_n^O = aA^O = aA_v^O + aA_n^O \tag{2}$$

Because of the slightly different sample size and column conditions, a different factor, b, will apply to the gas chromatogram of the weathered oil, ^{W}, and

$$M^W = M_v^W + M_n^W = bA^W = bA_v^W + bA_n^W \tag{3}$$

If the nonvolatile portion does not change appreciably on weathering, then $M_n^O = M_n^W$, and since $M_n^O = aA_n^O$, and $M_n^W = bA_n^W$,

$$aA_n^O = bA_n^W \tag{4}$$

and

$$\frac{b}{a} = \frac{A_n^O}{A_n^W} \tag{5}$$

The portion of oil, P, remaining on weathering is

$$P = \frac{M^W}{M^O} = \frac{bA^W}{aA^O} \tag{6}$$

and, substituting Equation 5 in Equation 6,

$$P = \frac{M^W}{M^O} = \frac{A^W}{A^O}\left(\frac{A_n^O}{A_n^W}\right) \tag{7}$$

In the calculation of the portion of oil remaining after the weathering of Navy distillate fuels by means of Equation 7, the volatile portion was considered the portion boiling below 298°C and the nonvolatile portion that boiling above 298°C. The results obtained are shown in Table 4. The calculated results were generally somewhat high. Because some of the nonvolatile portion will nevertheless evaporate, it would be expected that the values of A_n^W would be somewhat low and that P would be somewhat high. The results were especially high for the initial 6-week experiment with Oil C, giving a value of 0.781 for the portion remaining, whereas the recovery of the oil was 74.7%. In this longer evaporation, a higher proportion of the nonvolatile hydrocarbons were probably lost.

For residual fuels or for crude oils, Equation 7 cannot be used, because the higher boiling components are not completely recovered in the gas chromatography. For the evaporation of crude oils, Sivadier and Mikolaj therefore developed a more complicated equation which involves the areas between the C_{17} and C_{28} hydrocarbon peaks, comprising components boiling between 300°C and 431°C [7]. These ''truncated residues'' are assumed to be nonvolatile and their areas, A_{tr}, are used analogously to A_n to establish the proportionality between the area factors, b/a, of the gas chromatograms. Their equation for the weight fraction of oil evaporated, F, also includes the portion of volatiles originally present in the oil, Q_v^O, as determined by distillation up to 288°C:

$$F = Q_v^O\left(1 - \frac{A_{tr}^O/A_v^O}{A_{tr}^W/A_o^W}\right) \tag{8}$$

The evaporative weight losses calculated from the gas chromatographic data and the losses obtained from direct weighing of oil samples evaporated in dishes in the laboratory agreed within 1%.

The above agreement was better than that obtained for the Navy distillate fuels by use of Equation 7. This may be due partly to the fact that the ''truncated residuum'' was much larger and of higher average

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boiling point than the nonvolatile portion of the distillate fuels. It may also be due partly to the fact that the percent losses from the crude oils were generally much smaller than the percent losses from the distillate fuels.

In a manner analogous to the derivation of Equation 7, it is possible to derive the following equation for the portion retained, R, of any particular hydrocarbon during the weathering:

$$R = \frac{C_x^W}{C_x^O} = \frac{H_x^W}{H_x^O} \left(\frac{H_{18}^O}{H_{18}^W}\right) \tag{9}$$

Here C is the amount of a particular hydrocarbon present originally and after weathering, and H is the peak height of that hydrocarbon and of another hydrocarbon that is assumed to be nonvolatile. Octadecane (C_{18}) is the hydrocarbon that is assumed to have negligible volatility and the ratio in parentheses is a measure of the ratio, b/a, between the overall sensitivities of the two gas chromatograms. Actually, octadecane does evaporate to some extent, and the calculated R is a comparative portion retained as compared to the portion of octadecane retained.

The comparative retentions of the normal alkanes from dodecane (C_{12}) to heptadecane (C_{17}) in the simulated weathering of Oils C and D are shown in Figure 7. The effect of omitting the wind in the weathering of Oil D and the effect of much longer weathering of Oil C are also shown. The comparative retentions of the hydrocarbons decrease markedly as their size and boiling points decrease. Furthermore, these differences in retention are markedly increased for any particular oil as the degree of weathering is increased.

The curves of the comparative retentions also show that appreciable amounts of C_{16} and C_{17} hydrocarbons are lost, as compared to C_{18}. With increased weathering, it would be expected that increasing amounts of C_{18} and higher hydrocarbons would be lost and that increasingly higher hydrocarbons would have to be used as reasonably valid internal standards for gas chromatographic comparisons. For mild weathering, the approximation that certain hydrocarbons are nonvolatile may give adequate mathematical comparisons; but for severe weathering, the same approximation may not be suitable. Because the distillate fuels in some cases have very small amounts of components higher than C_{18}, they do not contain good internal standards.

Smith and MacIntyre used an equation very similar to Equation 9 to calculate the percentages of various normal hydrocarbons that remained in oil spills after various periods of time, using the C_{20} peak rather than the C_{18} peak as a reference [2]. Qualitative trends were established in the evaporation of the various hydrocarbons, but it was difficult to ascertain accurate peak values. Calculations of the loss of volatiles (up to C_{15}) were also made, but there was no possibility of measuring actual losses for comparison.
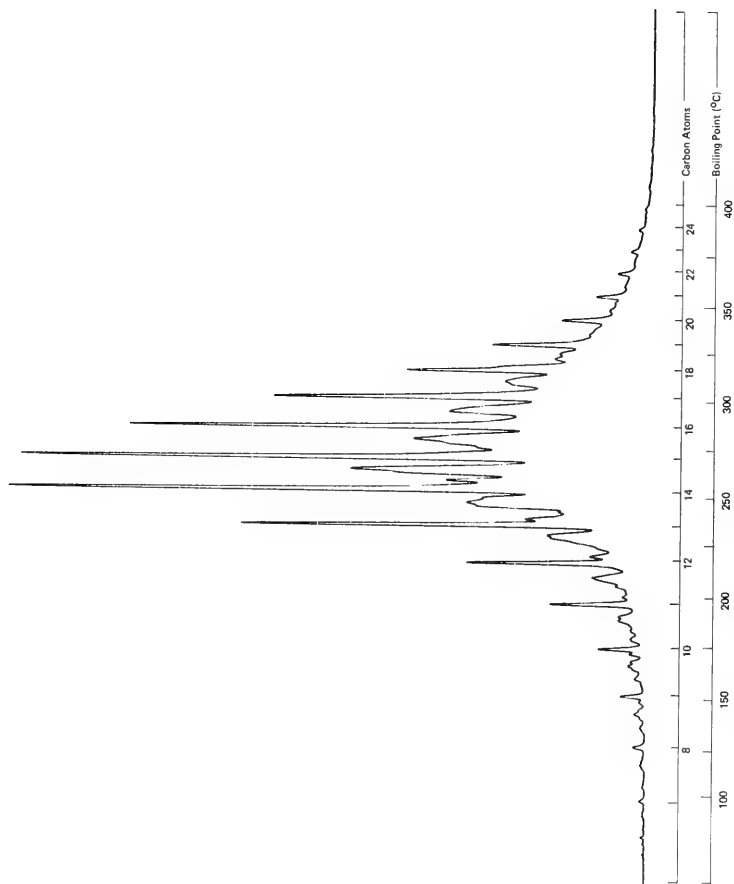
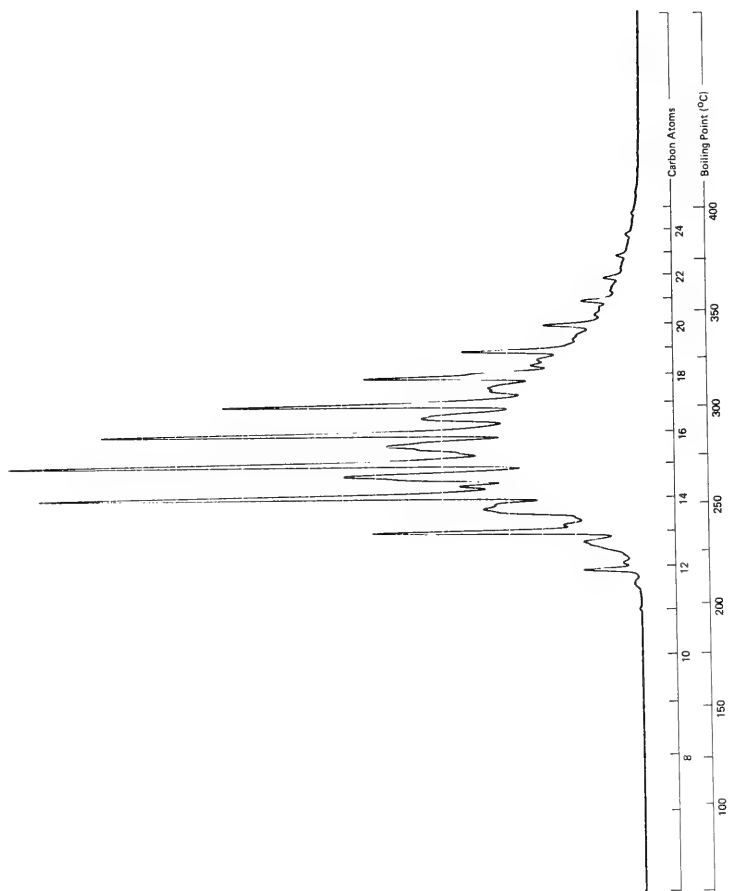Figure 1a. Gas chromatogram of original Fuel Oil A.

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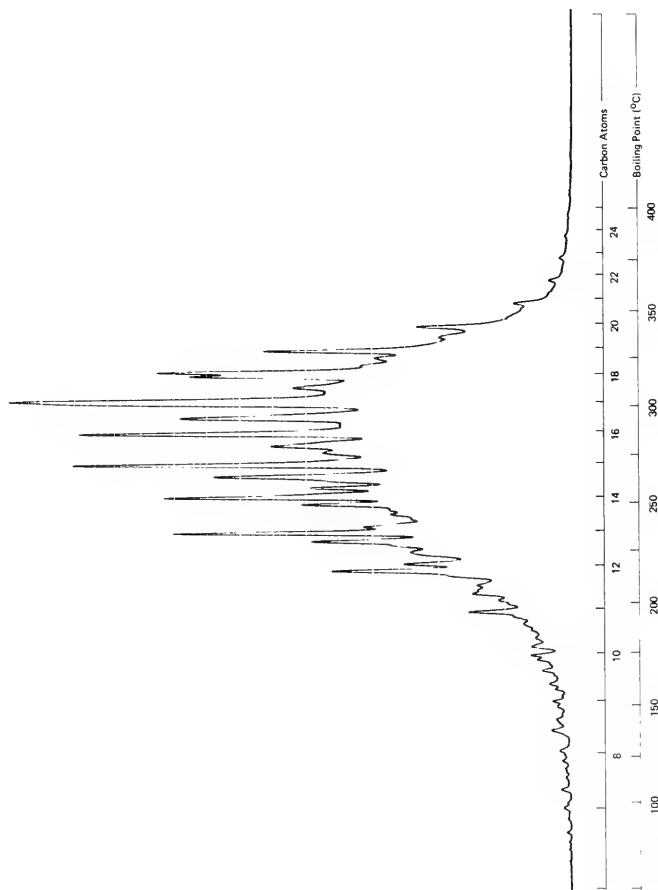Figure 1b. Gas chromatogram of weathered Fuel Oil A.
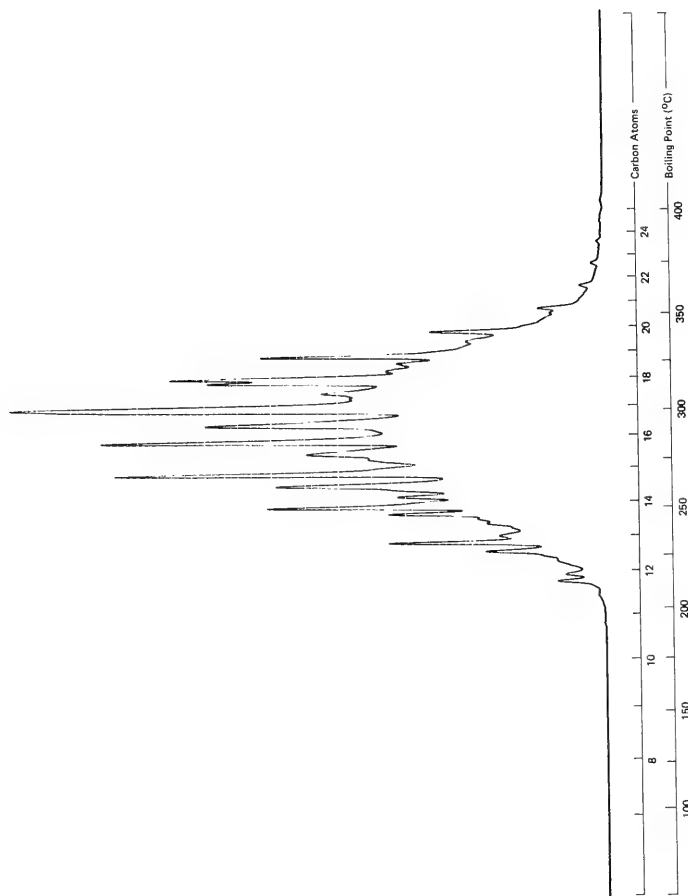
Figure 2a. Gas chromatogram of original Fuel Oil B.

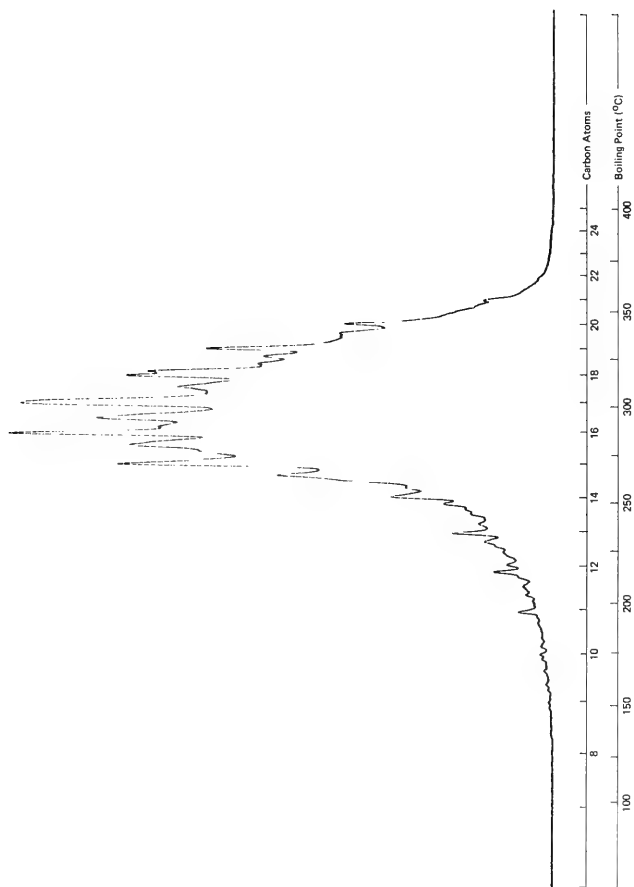Figure 2b. Gas chromatogram of weathered Fuel Oil B.

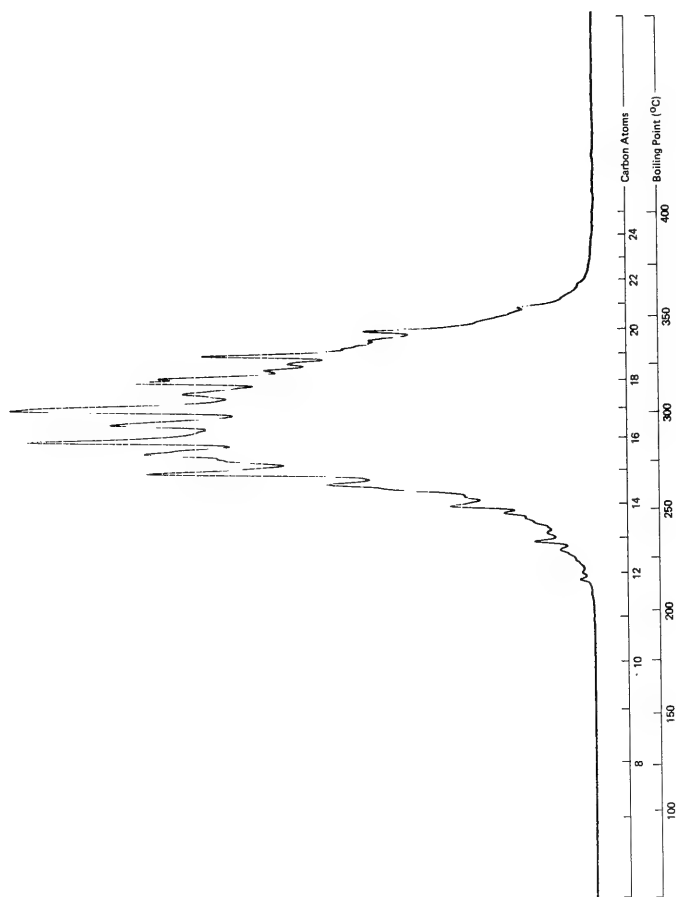Figure 3a. Gas chromatogram of original Fuel Oil C.

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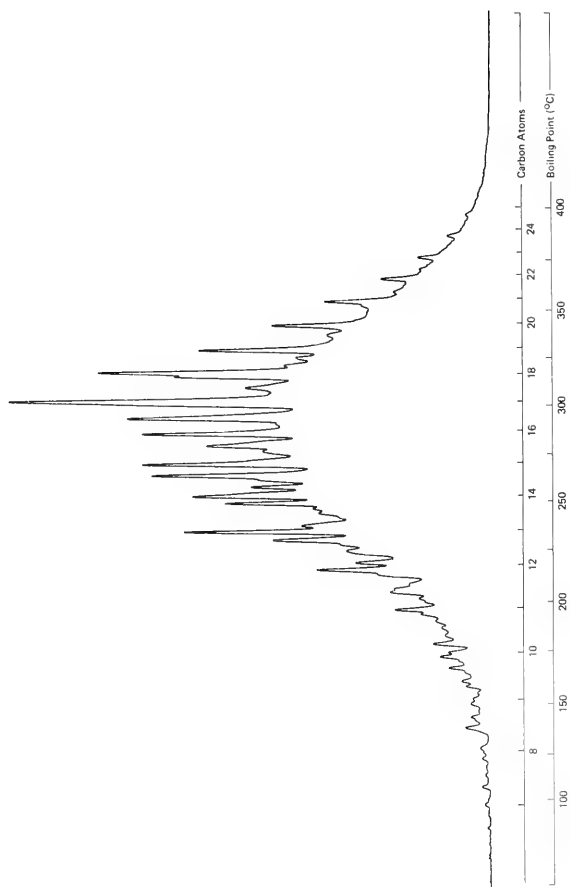Figure 3b. Gas chromatogram of weathered Fuel Oil C.
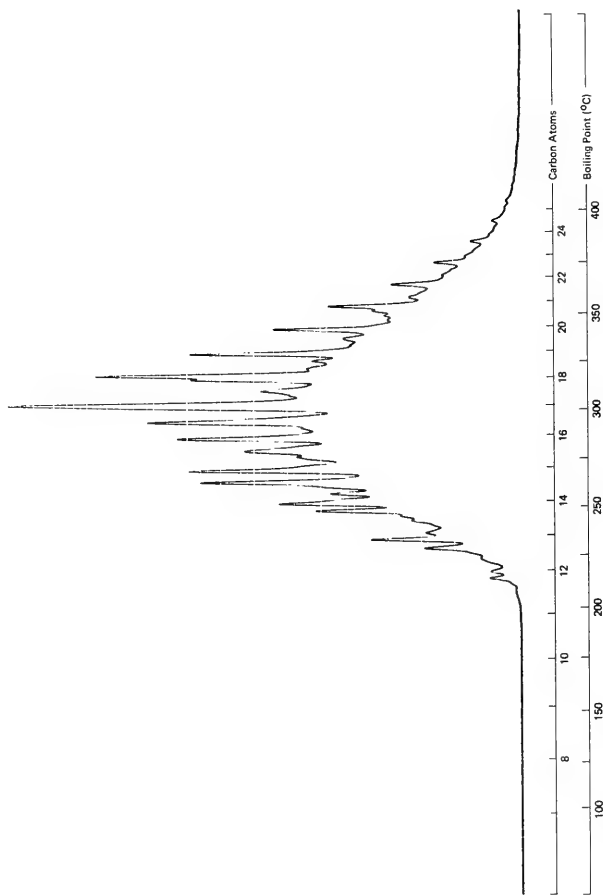
Figure 4a. Gas chromatogram of original Fuel Oil D.

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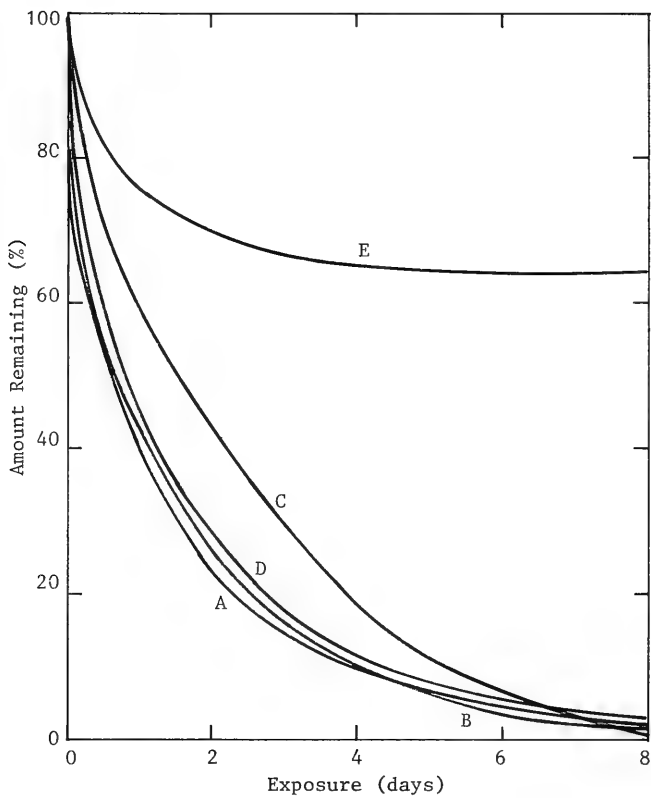Figure 4b. Gas chromatogram of weathered Fuel Oil D.

Figure 5. Evaporation of thin films of fuel oils.
(Oils A through E exposed in a stream of air.)

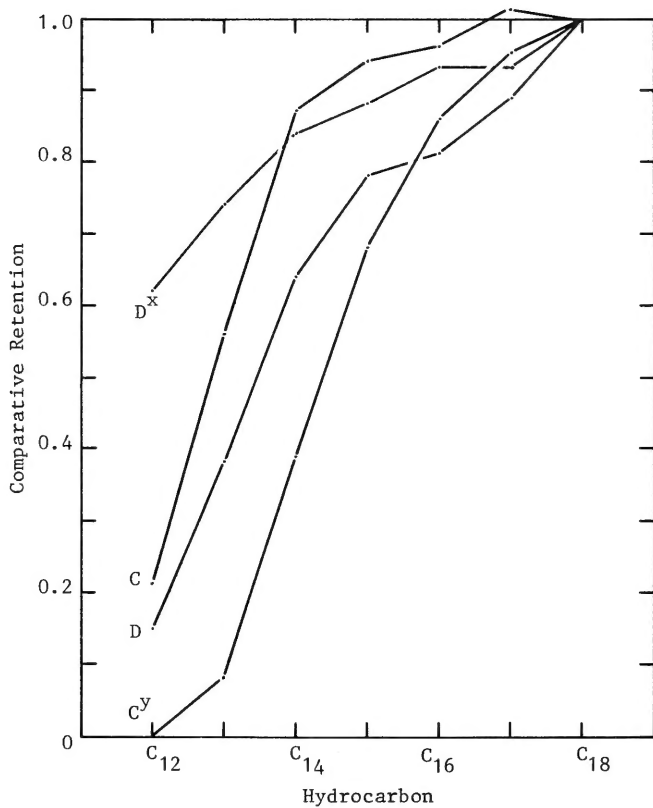Figure 6. Apparatus for simulated weathering.

Figure 7. Comparative retention of-low boiling hydrocarbons.
(For Oils C and D weathered one week, Oil C^y
weathered six weeks, and Oil D^x weathered without
wind.)

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